JOURNAL OF MATERIALS SCIENCE 19 (1984) 3325–3329

Electrical transport and semiconductor-semi-metal transition in $LaVO_4$

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The electrical conductivity (σ), and thermoelectric power (S) (300 to 1200 K), magnetic susceptibility (χ) (300 to 900 K) and DTA and TGA (300 to 1200 K) together with X-ray diffraction studies are reported. At room temperature the lattice is orthorhombic. The DTA study shows a broad peak around 1173 K indicating a possible structural phase transition of the compound. Practically no weight loss was observed in TGA from 300 to 1200 K. The electrical conductivity exhibits an exponential increase up to 855 K and between 855 and 885 K, it then jumps by a factor of 5×10^4 and remains practically constant up to 1200 K, indicating a transition from semiconducting to the metallic state around 870 K. S values remain positive throughout the temperature range studied indicating electrons to be the main charge carrier. In the semiconducting state (300 to 855 K) the plot of S against T^{-1} is linear with a slope of 0.04 eV against the activation energy of 0.83 eV. It has been shown that conduction is due to hopping of holes from V^{4+} defect centres to V^{5+} normal sites. The defects exist due to a small oxygen deficiency. The semiconductor semi-metal transition appears due to the overlapping of vanadium 3d and oxygen 2p bands around 870 K.

1. Introduction

Mixed oxides of rare earth and iron group elements are well known for their wide ranging physical properties. Among them vanadates of rare earths (RVO_4, R standing for La–Lu) form a group of compounds exhibiting interesting structural and magnetic transformation [1]. Recently, we reported the unusual magnetic behaviour of gadolinium [2], light [3] and heavy [4] rare earth vanadates at higher temperatures. These unusual results, which have been explained as being due to thermal generation of V^{4+} defect centres, indicate the interesting electrical transport properties of these compounds. Prompted by the above fact, and hoping that the nature of the defects and their mobility could be better understood by electrical transport studies, we decided to undertake a study of this in the whole series of rare earth vanadates. As our first attempt we present our studies on $LaVO_4$ in this paper. $LaVO_4$ is a diamagnetic compound with negative susceptibility at room temperature but it becomes positive around 525 K and increases in the positive direction with further increase in temperature. Our structural studies show that it has an orthorhombic unit cell at room temperature, unlike the tetragonal unit cell for all other compounds [5, 6].

2. Material preparation and experimental techniques

The details for the preparation of $LaVO_4$, including the starting materials, have already been reported in our earlier publication [3]. The X-ray diffraction pattern was recorded for a powdered sample using $CuK\alpha$ radiation. DTA and TGA studies were performed at a cooling rate of $10°\,C\,min^{-1}$, and the electrical conductivity (σ) and thermoelectric power (S) measurements were carried out using the sample holders and procedure described in several previous publications of our group [7–10].

3. Results and discussion

Measurements of σ and S were performed on

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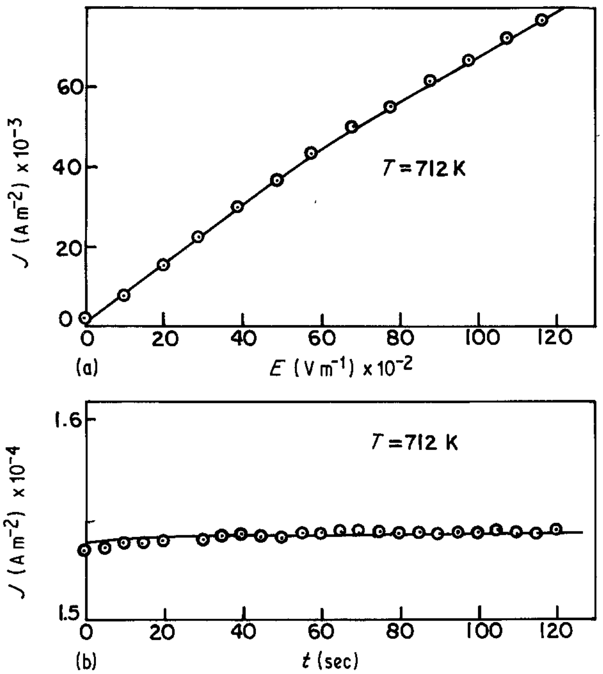

Figure 1 Plot of (a) current density (J) against applied electric field (E), and (b) current density (J) against time (t) for $LaVO_4$ at 712 K.

pressed pellets because of the difficulty of growing large single crystals of the compound needed for these measurements due to its high melting point and our limited facilities. In the pellets, grain boundaries and air pores considerably reduce conductivity and often measurements on them do not reflect the bulk value for the material. It is not possible to eliminate the defects in pellets; however, they can be prepared in such a way that these effects are considerably reduced and in such a situation the bulk value for the material can be obtained employing a suitable correction. The first requirement is to make pellets of uniform density. This has been achieved using a proper die and keeping the (t^2/A) ratio (where t is the thickness and A the face area of the pellet) less than four as fixed by other workers [7–11]. Air pores are considerably reduced if these uniform pellets are made using fine grained powders at a higher pelletizing pressure (P). This conclusion has been drawn by measuring the density of pellets (d_p) at different pressures (P). d_p increases with P and tends to approach a constant value when the latter exceeds $6 \times 10^8\, \mathrm{N\,m^{-2}}$. However, the maximum value of d_p achieved is only about 90% of the X-ray density of the material. The same trend in variation is observed in electrical conductivity with P. We used pellets made at $P > 6 \times 10^8\, \mathrm{N\,m^{-2}}$ for further studies. The pellet conductivity values (σ_p) are further corrected for the bulk value of electrical conductivity (σ) using the following relation [12]

$$\sigma = \sigma_p \left[1 + \frac{f}{1 + f^{2/3}}\right] \qquad (1)$$

where

$$f = \frac{d_0 - d_p}{d_0} \qquad (2)$$

is called the pore fraction. S values are little affected by P; however, they are slightly less for pellets fabricated at higher P. This decrease is little larger than the error (± 5%) involved in the measurement of S. These values of S require little correction due to pore fraction (f), and therefore they have not been corrected. The electrical conductivity of highly pressed and well sintered pellets has also been measured as a function of frequency at a few fixed temperatures. It has been found to be almost independent of frequency indicating that grain-boundary effects are not very predominant. Ohmic contact between pellet and electrode interface is another stringent requirement for measurement of both σ and S. We used platinum foil electrodes for such measurements. To investigate the nature of the contact, d.c. current density (J) through the pellet was recorded as a function of electric field (E). The plot of J against E, shown in Fig. 1a, is almost linear indicating the ohmic nature of the contact. Fig. 1b shows a plot of J against time. It was found to be

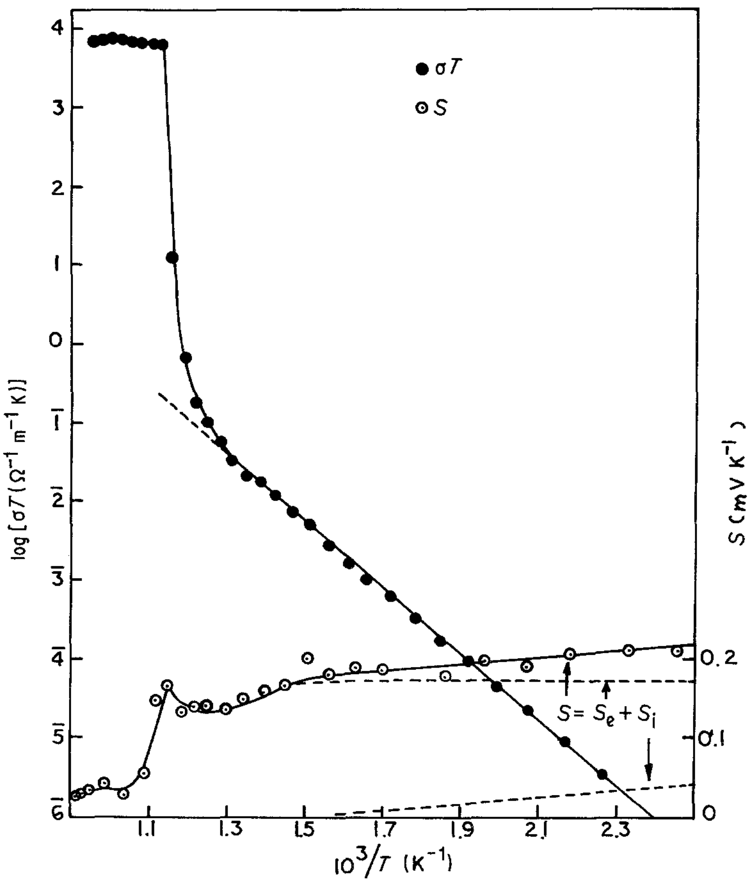

Figure 2 Plot of logarithm of the product of electrical conductivity and absolute temperature (log σT) and thermoelectric power (S) against the inverse absolute temperature (T^{-1}) for $LaVO_4$. S_e and S_i denote the extrinsic and intrinsic contribution to thermoelectric power.

almost independent of time indicating that the current is caused by electrons (or holes) but not by ions or their vacancies.

Both thermoelectric power and electrical conductivity of a few pellets have been measured at different temperatures. Fig. 2 shows a plot of log σT and S against the inverse temperature (T^{-1}) in the temperature range 385 to 1100 K. No hysteresis is observed and the curves are the same for both heating and cooling cycles. $LaVO_4$ is a semi-insulating compound with a room temperature conductivity of $6.0 \times 10^{-12}\,\Omega^{-1}\,m^{-1}$. The plot of log σT against T^{-1} is linear in the temperature range 385 to 855 K. Around 870 K, there is sharp increase in log σT and at higher temperatures the plot becomes flat. Around 870 K, the electrical conductivity of the compound jumps from $1.53 \times 10^{-4}\,\Omega^{-1}\,m^{-1}$ just below this temperature to $7.08\,\Omega^{-1}\,m^{-1}$ just above it, an increase of about 5×10^4 within a temperature interval of 30 K. The curve below 870 K can be represented by the equation

$$\sigma T = 1.06 \times 10^4 \exp\left(-\frac{0.83\,\text{eV}}{kT}\right) \qquad (3)$$

The plot of S against T^{-1} is linear from 385 to 715 K. It shows a peak around 870 K and then drops and becomes flat. Below 715 K its variation with T can be represented by the relation

$$S = \frac{0.04\,\text{eV}}{eT} + 0.12\left(\frac{\text{mV}}{\text{K}}\right) \qquad (4)$$

Fig. 2 shows that S remains positive throughout the temperautre range studied indicating that the dominant charge carriers of electric current are negatively charged particles. The variation of d.c. electrical conductivity with time (Fig. 1b) indicates that current is electronic in nature. These observations show that the dominant charge carriers of the electric current in this solid are electrons. Looking at the plot of log σT against T^{-1} (Fig. 2) one can divide the conduction range into two regions: (a) a semi-conducting region from 385 to 855 K; and (b) a metallic region above 870 K. The transition from the first region to second region takes place around 870 K, which may be referred to as the transition temperature.

First, let us try to understand the conduction mechanism below the transition temperature

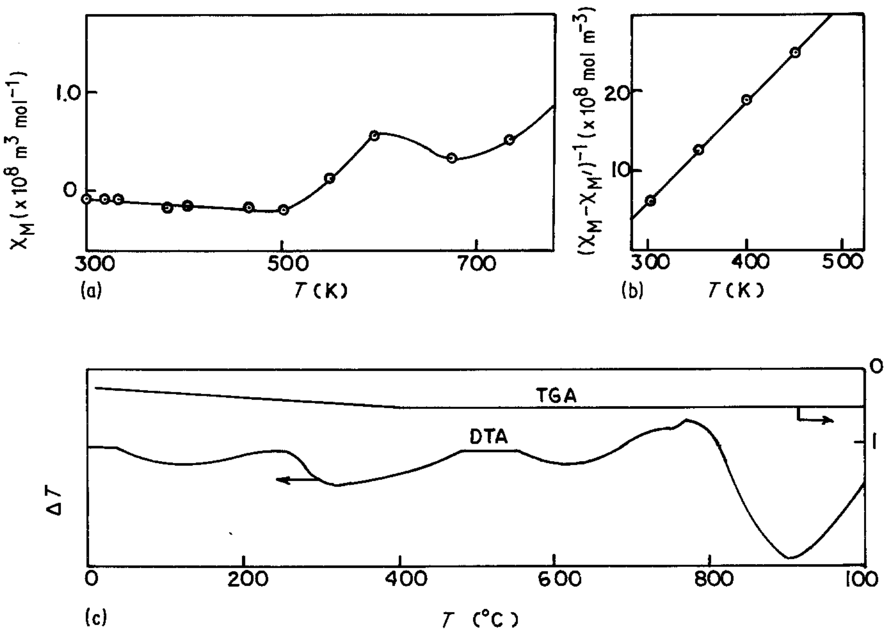

Figure 3 Plots of (a) molar magnetic susceptibility (χ_M) and (b) the difference between the measured molar magnetic susceptibility and the diamagnetic value of molar susceptibility ($\chi_M - \chi_M'$). (c) DTA and TGA curve with temperature (T).

($T < 870$ K). The conduction may be either band type or hopping type. In the former type the relevant bands which may be important are empty La^{3+}: 5d, V^{5+}: 4s, V^{5+}: 3d and the completely filled O^{2-}: 2p band. Both the 5d and 4s bands are normally expected to lie above the 3d band. Thus the valence and conduction bands in this material will be formed by oxygen 2p and vanadium 3d bands. The intrinsic conduction, therefore, will be due to holes in the 2p band and electrons in the 3d band. In such a situation the dominant charge carrier for mobility is expected to be holes. However, the dominant charge carriers in this material are electrons. This argument does not favour intrinsic band conduction as the dominant process in this material. Donor centres having a large ionization energy (1.86 eV, evaluated from plots of log σ against T^{-1} not shown in the figure) are not expected. Thus in the semi-conducting range, the conduction in this material is of the extrinsic hopping type. The existence of a small amount of paramagnetic impurities is also indicated by our susceptibility studies as shown in Fig. 3a. Here χ_M increases in the negative direction against the expected results of a temperature-independent diamagnetic susceptibility. This has been explained by us [2] as being due to the existence of a small amount of paramagnetic impurities whose contribution decreases with temperature and in turn $LaVO_4$ tends towards a diamagnetic value. We do not expect to find a significant amount of chemical impurities, because the starting materials for the fabrication of this compound were relatively pure. A slight oxygen deficiency, however, may lead to the formation of V^{4+} centres. We believed that a small number of V^{4+} centres do exist in all vanadates, and conduction in the semiconducting range is due to the hopping of electrons from V^{4+} to the neighbouring V^{5+} centres. The thermoelectric power in such a situation will be given by the relation [13, 14]

$$S = \frac{k}{e}\left(\frac{S_R^*}{k} - \log\frac{C}{1-C}\right) \tag{5}$$

where S_R^* is the effective entropy of the lattice, which is temperature independent, and $C = n/N_S$, where n and N_S are the densities of defects and normal sites, respectively. Usually S_R^*/k is negligibly small and can be omitted. This reduces the above formula to the following relation

$$S = \frac{k}{e}\left[\log\left(\frac{N_S}{n} - 1\right)\right] \tag{6}$$

In the context of rare-earth vanadates, N_S and n will be the number of V^{5+} and V^{4+} ions per unit volume, respectively. An estimation of the number of V^{4+} centres can be made from susceptibility data. Using the relation

$$n = \frac{3kC}{\mu_\beta^2 \mu_0 p^2} \qquad (7)$$

where C is the inverse of slope of the plot of $(\chi_M - \chi'_M)$ against T (χ_M and χ'_M are the observed and diamagnetic molar susceptibilities of the compound), p is the effective magneton number for a V^{4+} ion and μ_β, μ_0 and k are Bohr magneton, permeability constant and Boltzmann constant, respectively. This gives $n = 5.5 \times 10^{21}\,\mathrm{mol}^{-1}$. Using this value, S is found to be $0.175\,\mathrm{mV\,K}^{-1}$. This is just about the same value as that obtained experimentally. Heikes' formula gives a temperature-independent value of thermoelectric power. However, it has a slight temperature dependence and the curve of S against T^{-1} is linear with a slope of 0.04 eV. This is because of the contribution coming from intrinsic conduction. Both contributions are shown separately in Fig. 2. The conductivity jumps by a factor of 5×10^4 around 870 K and above becomes $\sim 7.08\,\Omega^{-1}\,\mathrm{m}^{-1}$, a typical value for semi-metals. Thus this transition can be termed semi-conductor–semi-metal transition. Fig. 3c shows a DTA plot for this material. No discontinuity is observed around 870 K, indicating that there is no change in crystal symmetry around this temperature. However, a drop is seen around 533 K and also a broad peak around 1173 K. This peak reflects the same structural change. The first temperature is close to 525 K at which the susceptibility of this material changes from negative to positive. This change is possible only when some negative ions are thermally generated. In this respect it is worth noticing that the VO_4 tetrahedron in RVO_4 is slightly distorted and it is possible that the V–O linkage may not be perfectly ionic but partially covalent. The vanadium ion, then, is expected to exist in an intermediate ionic state between V^{5+} and V^{4+} and hence may contribute to the susceptibility. The covalency increases with temperature. This means that as the temperature rises the oxygen 2p wave function may hybridize with the 3d wave function. Probably this hybridization is achieved around 870 K. The overlapping of the 2p and 3d wave functions means the compound is metallic. The criterion for this to occur is $2J/I \simeq 1.15$ [15], where $2J$ is the band width of the 3d (split lower) band and I is the interatomic interaction energy. Thus the transition from the semiconductor to the semi-metal state in the material is due to the 3d–2p band overlap without any symmetry change in the crystal.

Acknowledgement

One of the authors (KG) thanks CSIR for financial assistance. We would like to thank Dr D. C. Agrawal, IIT, Kanpur for DTA and TGA studies and Dr R. Nagarajan, National Chemical Laboratory, Pune for recording the X-ray diffraction pattern.

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Received 24 November 1983
and accepted 10 January 1984